This precipitous decrease may correspond with the entry into region II of Fig. 68.

The fact that the increase of tensile strength when the temperature from which cooling occurs rises above Ac_1, is very much more marked when the cooling occurs in the air than when it takes place still more slowly in the furnace itself, certainly suggests that even air cooling may be rapid enough to cause a certain degree of hardening proper by preventing the change from austenite into pearlite with ferrite or cementite from really completing itself.

While further investigation on this point is desirable, Dr. Campbell's series cooled in lime and in the furnace respectively show a material increase of tensile strength, too regular and consistent to be referred to experimental errors, and hardly to be referred to hardening proper.

Dr. Campbell's data in Table 13 do not indicate that finishing temperature has any marked influence on tensile strength, probably because his finishing temperatures were limited to the rather narrow range between 669° and 963° C.

This small influence of the temperature from which slow cooling occurs on tensile strength agrees with Prof. Sauveur's* early determinations of the relation between the grain-size and tensile strength of rail steel; although here, too, it is to be noted that the range of temperature represented is probably very narrow and that his data gave indications that, with a little higher finishing temperature, the tenacity increased, somewhat as is shown in Fig. 79d.

The Heat-treatment of Cast Iron.

220. THE HEAT-TREATMENT OF CAST IRON. — The reactions normal to the freezing range (1) to (6) inclusive, and those normal to the critical or transformation range (7) to (13) inclusive, suffice to explain the results obtained in the industrial heat-treatment of cast iron, if we remember that those of the critical range take an appreciable time, that those of the freezing range are completed only slowly, and that reaction (10), the transformation of graphite and austenite into cementite, is extremely slow. It is through playing upon the lag of these reactions, through

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* *Loc. cit.*

permitting the several reactions to occur to the extent desired but no farther, that we vary the properties of cast iron by heat-treatment.

Let us now take up certain of these processes of heat-treatment, including among them the faster or slower initial cooling of the cast iron as it runs from the blast-furnace or the foundry cupola-furnace, yielding whiter and harder, or grayer and softer cast iron. Let us then consider (1) the chilling of cast iron in the process of making chilled castings, and (2) that of annealing those castings; and finally (3) the process of making malleable cast iron castings.

To fix our ideas, let us consider the case of cast iron containing 4.00 per cent of carbon.

221. THE REACTIONS WHICH SHOULD THEORETICALLY OCCUR IN FREEZING AND COOLING OF SUCH A CAST IRON. — It is not necessary to recapitulate these, because they have already been fully set forth. But, to present this and kindred matter in a condensed form to the eye I have prepared the tabular part of Fig. 68, arranging it so that it conforms with the several regions of that figure, as applied to a cast iron containing 4.00 per cent of carbon. In this table the reactions which are supposed to occur in the several regions are indicated in *italics,* and the constituents which are supposed to be present in each region are shown in CAPITALS.

The theoretical reactions in the freezing and cooling of such a cast iron are set forth in column 1.

There are three deviations (of which two are set forth in columns 2 and 3 of Fig. 68) from this theoretical set of reactions, which we may now consider. These deviations are as follows:

(1) that which we may call the formation of typical gray cast iron, the combined carbon of which is just the quantity (say 2 per cent) which suffices to saturate the austenite when in region VII;

(2) that which we may call the formation of typical white cast iron, in which all the carbon is combined (as cementite);

(3) and that which we may call the formation of typical ultra gray cast iron, in which all the carbon is in the state of graphite.

222. REACTIONS IN THE FREEZING AND COOLING OF TYPICAL GRAY CAST IRON. — By typical gray cast iron I refer to one in

which reaction (10), the transformation of graphite into cementite by reaction with austenite, is suppressed, but the other reactions take place in their entirety.

The result of this suppression is that the cast iron, when cold, contains in the form of cementite the carbon (assumed to be 2.00 per cent), which in region VII saturated the austenite, and as graphite the whole of the carbon which in region VII was present in the form of graphite, which by difference is also 2.00 per cent. In short, this cast iron when cold contains 2.00 per cent of combined carbon and 2.00 per cent of graphite.

The reactions, *etc.,* which, as we provisionally hold, occur in the cooling of such a cast iron, are set forth in column 2 of Fig. 68.

223. Reactions in the Freezing and Cooling of Typical White Cast Iron. — By typical white cast iron I mean one in which the whole of the carbon is present in the combined state, *i. e.,* as cementite; and this we may assume provisionally is due to complete suppression of reaction (3), *i. e.,* the separation of graphite in the freezing of the molten eutectic, so that for reactions (2) and (3) jointly there is substituted reaction (14). In other words in region VII the metal consists of supersaturated austenite, instead of the normal eutectic conglomerate of graphite plus saturated austenite. The whole of the carbon, which in region VII exists as austenite is in further cooling changed into cementite. This, and indeed the whole course of matters, is indicated in column 3 of Fig. 68.

224. Reactions in the Freezing and Cooling of Typical Ultra Gray Cast Iron. — By typical ultra gray cast iron I refer to one in which the general course of events is the same as in the genesis of typical gray cast iron, with the important exception that owing to the presence of silicon or to some other cause, the transformation of graphite is greatly stimulated, so that the whole of the carbon in the cast iron when cold is found in the condition of graphite, and the iron then consists of ferrite plus graphite alone. The reactions in its freezing and cooling are not shown in the tabular part of Fig. 68.

Just what takes place in the cooling of such cast iron, or of a cast iron which approaches this type in containing when cold less combined carbon than would have saturated the austenite in region VII, can at present only be conjectured. One possible course

is that the austenite which freezes out as the temperature sinks through region II is quite carbonless in case of this typical ultra gray iron, and unsaturated in case of cast irons which approach this ultra type. In the further cooling of such iron, the conditions may be the same as those which we have supposed above for typical gray as distinguished from ultra gray cast iron. That is to say reaction (10), which ought to convert the graphite on cooling from region VII into cementite on cooling from region VII into region VIII, is suppressed, with the consequence that the whole of the graphite which was present in region VII is found in the cold cast iron.

In case of typical ultra gray iron, because the austenite is supposed to be quite carbonless, the normal reactions (11) and (8) by which austenite is normally changed into a conglomerate of pearlite and cementite, by definition cannot occur; and instead the austenite is simply transformed into ferrite.

In case of cast iron which approaches this type, we may suppose that these reactions (11) and (8) take place normally, with the result that the metal when cold consists of the graphite formed in freezing, plus as much cementite as suffices to represent the carbon present in the austenite in region VII. If that austenite contained less than 0.90 per cent of carbon, in short was hypo-eutectoid, then the cold cast iron should be a conglomerate of (1) graphite, and (2) pearlite with (3) free or " excess " ferrite. But if that austenite contained more than 0.90 per cent of carbon, *i. e.,* was hyper-eutectoid, then the conglomerate of which the cold cast iron should consist, should contain free or " excess " cementite instead of free ferrite.

225. The Chilling of Cast Iron. — We have seen that in the freezing of a hypo-eutectic cast iron, first austenite, a solid solution of carbon in iron, freezes out, reaction (2), and second the eutectic (austenite plus graphite), freezes, reaction (3). We have further seen that the proportion of graphite which is actually found is the greater the slower the cooling, within limits; so that a sudden cooling appears to restrain the splitting up of the mother-metal into austenite plus graphite, leaving the austenite supersaturated with carbon, just as in the case of steel it prevents austenite from breaking up into pearlite. Thus sudden cooling retains in each case a supersaturated solution of carbon in iron, supersaturated austenite, which appears to follow the general rule that austenite is the harder the more carbon it contains.

Now we often purposely hasten the cooling of cast iron by casting it in cold iron moulds, a process known as "chilling," to distinguish it from the still more sudden cooling which quenching in water gives, as in the hardening of steel. Chilled cast iron is intensely hard and also very brittle. In this operation we probably get highly supersaturated austenite, first by restraining its tendency to resolve itself into graphite and saturated austenite at the eutectic freezing-point *aBc*, reaction (3), and second by preventing the austenite thus preserved from splitting up into pearlite plus cementite in crossing and leaving the transformation region VIII at Ar₁, *PSP'*.

Much the same applies to hyper-eutectic cast iron; the sudden cooling should restrain both the separation of graphite in freezing, thus giving highly supersaturated austenite, and also the transformation of this austenite into pearlite and free cementite in crossing and leaving region VIII.

226. THE ANNEALING OF CHILLED CASTINGS. — Chilled castings unannealed are too brittle for many purposes, such as railroad car-wheels. They are annealed by heating them to a dull red heat, at which the supersaturated austenite splits up into pearlite plus cementite, *i. e.,* undergoes the transformation which it would have undergone in region VIII had the cooling been slow.

But even when thus annealed the chilled castings are white in fracture, and intensely hard. Why is this? Had the freezing been slow the austenite would have been only saturated, *i. e.,* would have contained only some 2 per cent of carbon, and the rest of the carbon would have existed as graphite. When such saturated austenite is resolved into pearlite in region VIII it yields only

$$2 \times \frac{100}{6.67} = 30 \text{ per cent of cementite, together with 68 per cent of}$$

ferrite (together with the accompanying 2 per cent of graphite). But our supersaturated austenite, containing let us say 4 per cent of carbon dissolved in it, on splitting up in region VIII yields 60 per cent of cementite plus 40 of ferrite, in short twice as much cementite. Now, as cementite is intensely hard while ferrite is very soft, we have here a clear explanation of the greater hardness of chilled than of slowly cooled castings. And in the absence of graphite we have an explanation of the white fracture.

Were it possible to cool our molten cast iron extremely rapidly past regions II and VII, say to 800° in region VIII, and then

cool it slowly past Ar₁, we should doubtless get approximately the hardness which we get in our chilled castings when they have been annealed. But in actual practice we split the operation up into two, a complete cooling (chilling) followed by reheating (annealing) as a matter of convenience.

Here as in case of steel, the annealing relieves the stress due to the initial sudden and hence unequal cooling.

Since it is only the tread of a car-wheel that needs hardness, so that it may resist wear, and since chilled, *i. e.,* white cast iron, is relatively brittle even after annealing, such objects are cast in moulds made partly of sand and partly of cold iron, so that the tread of the wheel is chilled and remains white and rich in cementite, while the rest of the wheel cools slowly and is not chilled, *i. e.,* is gray in fracture. We thus get the tread intensely hard because of its large proportion of cementite, but the "plate" or interior of the wheel is in the relatively ductile and safe state of gray cast iron, in which much of the cementite is replaced by a mechanical mixture of ferrite and graphite.

As this process is actually practiced, the chilled wheels are removed from their moulds when all but the very tread is still red-hot, and are then transferred to a pit in which they are allowed to cool down very slowly. The tread, in this operation, is reheated by the heat present in the body of the wheel when transferred to the annealing pit.

When very massive pieces of cast iron, such as large rolls, are chilled, no special annealing is required, because such castings, from their very size and shape, cool with sufficient slowness through VIII and the upper part of region IX to permit the austenite to resolve itself into pearlite and cementite. The rate of cooling is fast enough to restrain the very slow graphite-forming reaction (3), but is it not so fast as to arrest the transformation of austenite into pearlite and cementite, reactions (11) and (8).

227. MANUFACTURE OF MALLEABLE CASTINGS. — In the manufacture of malleable castings we use a white cast iron, *i. e.,* one which in solidifying at the usual relatively rapid rate generates within itself only very little graphite. It thus contains an abnormally great proportion of cementite. These white cast iron castings are then "annealed" by heating them for days to a temperature probably in region VII (say 1000°), so that the graphite, which would have separated in sufficiently slow freezing, has a chance to

form; and we remove part of this graphite by means of iron oxide in a bed of which these castings are heated. The reaction is of the following type:

$$Fe_3O_4 + C = CO + 3FeO.$$

As the carbon at the very skin of the casting is thus removed, that within diffuses outwards to take its place. We may suppose that the actual diffusion is of the carbon in the solid-solution or austenite state; that this diffusion and the change of its carbon from the dissolved to the free or graphitic state occur side by side; and that it is this free graphite which is directly attacked by the iron oxide.

We may regard these castings as in effect a variety of gray cast iron, but with the special advantage over the common gray iron that the particles in which the graphite forms when the metal is thus reheated into region VII are extremely fine, and therefore much less injurious, less weakening and less embrittling, than the coarse flakes of graphite which form in regions II and III, in the freezing of the molten metal. The graphite generated in the solid metal in region VII has no opportunity of coalescing into flakes, as that does which is generated in the passage from the molten to the solid state; it remains as an impalpable powder.

Besides being less injurious, this finely divided graphite is also susceptible of being removed in considerable part, especially from the very outside of the casting, by surface oxidation, which is not the case with the coarse graphite flakes of common gray cast iron.

We may call this finely divided graphite " temper graphite," a modification of Ledebur's name " temper carbon."

These castings are relatively cheap like cast iron, not so much because the cost of conversion into steel is avoided, — indeed for this conversion has to be substituted the long annealing process by which the cementite is changed into temper graphite; — but because the lower melting-point of the metal as a whole greatly lessens the foundry expenses. At the same time these castings avoid the weakness and brittleness of white cast iron due to its great proportion of cementite, and they avoid the weakness and brittleness which the large size of the graphite flakes in common gray cast iron causes.

CHAPTER X. — THE PHASE RULE

228. IN GENERAL. — What is the Phase Rule? What is it about, and why is it of importance to metallurgists? The answer to these questions will be made easier by refreshing our memory on certain elementary matters.

We have seen that, just as crystalline rocks are composed of perfectly definite and distinct mineralogical entities called minerals, such as the mica, quartz and feldspar of a granite, so our alloys when solid are in general composed of similar definite entities, which correspond to the minerals of our crystalline rock. These entities, these minerals in one case and quasi-minerals in the other, are called " Phases," a term which will be more closely defined later. The phase rule has to do with these phases.

We have further seen that these microscopic constituents actually present in an alloy may or may not be those which should normally be present at the existing temperature. For instance we have seen that the constituents normal to slowly cooled steel are ferrite and cementite, partly free, partly mechanically mixed as the quasi-eutectic conglomerate called pearlite. We have further seen that, if the steel is cooled suddenly from above the critical range, instead of consisting when cold of these normal constituents, it actually consists chiefly of austenite. The austenite is not normal at this temperature; it exists normally only at temperatures in and above the critical range; but it may be preserved by sudden cooling; when so preserved it is abnormal, and in this sense the suddenly cooled steel is not in molecular equilibrium.

The phase rule is one which by superior analysis, and almost by inspection, helps us to answer such questions as (1) whether in any given alloy the constituents actually present are those which ought normally to be present, *i. e.*, whether the alloy is in molecular equilibrium in this sense; and (2) for any given transformation or change of state, what are the normal constituents which ought to result, *i. e.*, which correspond to equilibrium in this sense; and (3) many other related questions.

This it does essentially through telling us the " degree of liberty " of the alloy regarded as a system, *i. e.*, whether the ex-